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Article

(*R*)-(−)-Carvone and (1*R*, 4*R*)-*trans*-(+)-Dihydrocarvone from *Poiretia latifolia* Vogel

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Os óleos essenciais de folhas de *Poiretia latifolia* Vogel nativas e cultivadas (amostras A e B, respectivamente) e de flores nativas (amostra C), foram obtidos por hidrodestilação e analisados por CG, CG/EM, e através de cromatografia gasosa em fase quiral (CGFQ). Vinte e quatro componentes foram identificados, representando 99,25, 99,26 e 99,23% dos óleos, respectivamente. Os maiores constituintes dos óleos foram os monoterpenos (*S*)-(−)-limoneno (16,05, 27,60, 15,60%, respectivamente), (1*R*, 4*R*)-*trans*-(+)-diidrocarvona (18,05, 0,66, 77,80%, respectivamente) e (*R*)-(−)-carvona (61,05, 64,20, 4,50%, respectivamente). Os óleos essenciais apresentaram uma atividade antimicrobiana moderada quando avaliados frente a bactérias e Gram-positivas, Gram-negativas e fungos.

The essential oils of *Poiretia latifolia* Vogel, native and cultivated leaves (Samples A and B, respectively) and native flowers (sample C), were obtained by hydrodistillation and analyzed by GC, GC/MS and chiral phase gas chromatography (CPGC). Twenty-four compounds were identified, representing 99.25, 99.26 and 99.23% of the oils, respectively. The major constituents of the oils were the monoterpenes (*S*)-(−)-limonene (16.05, 27.60, 15.60%, respectively), (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone (18.05, 0.66 and 77.80%, respectively) and (*R*)-(−)-carvone (61.05, 64.20 and 4.50%, respectively). The essential oils were evaluated against some strains of Gram (+) and Gram (−) bacteria, and yeast, but displayed only modest antimicrobial activity.

Keywords: *poiretia latifólia*, essential oil, antimicrobial activity, (*R*)-(−)-carvone, (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone

Introduction

Poiretia, a genus of the Papilionoidae-Leguminosae family, is found throughout the equatorial and subtropical regions of the Americas. In Brazil, it comprises about 12 species found in the Southwestern region.[1] *Poiretia latifolia* Vogel, locally called "erva-de-touro", is native to South America (Southern Brazil, Uruguay, Paraguay, and Argentina). In Brazil, *Poiretia latifolia* is generally used in popular medicine for the treatment of hemorrhoids, renal diseases, dysentery, and as an aphrodisiac.[2] As a continuation of our research on the essential oils of aromatic plants from the state of Rio Grande do Sul, we now report on the chemical constituents of the essential oils obtained from leaves and flowers of native and cultivated *P. latifolia.* The identification of the chemical constituents was based on comparison of their relative retention times and mass spectra with those obtained from authentic samples and/or the Wiley/Nist libraries and those published by Adams.[3] The stereochemistry of the main chiral compounds present in the oils (limonene, carvone and dihydrocarvone) was determined by chiral phase gas chromatography (CPGC), and by chemical reactions.

The oxygenated monoterpenes carvone and dihydrocarvone are potential inhibitors of bacterial,[4-6] fungal growth,[7] as well as prospective insect repellents.[8] The most important technical application of carvone is its use as a reversible suppressant of sprouting in stored potatoes or flower bulbs.[5] Carvone and dihydrocarvone have shown insecticidal activities against the rice weevil *Sitophilus oryzae* (L), one of the most widespread insect pests of stored cereals.[9] Carvone is present in the *S*-(+)-enantiomer

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in oils from caraway seeds (*Carum carvi*; 50-70% presence) and from dill seeds (*Anethum graveolens*; 40-60%), though it is not always pure.[10-12] (*R*)-(−)-carvone is the principal constituent in spearmint oil (*Mentha spicata*) and some oils, such as gingergrass oil, contain racemic carvone.[13] (*S*)-(+)-carvone is usually obtained from caraway seeds, while (*R*)-(−)-carvone is obtained from spearmint oil.

Biosynthetically, (*R*)-(−)-carvone is formed by cyclization of geranyl pyrophosphate to (−)-limonene, hydroxylation to (−)-*trans*-carveol and dehydrogenation to (−)-carvone.[14] According Croteau *et al.*[15] this transformation requires four enzymatic steps, including geranyl diphosphate synthase (prenyltransfer), limonene synthase (cyclization), cytochrome P450 limonene hydroxylase (oxygenation) and carveol dehydrogenase (redox transformation). On the other hand, (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone might be derived from (*R*)-(−)-carvone, in which the C=C bond is reduced enantioselectively to dihydrocarvone.[16]

Experimental

Plant material

Native *Poiretia latifolia* was collected in the town of São Pedro do Sul, RS, Brazil (29º 37' 14'' S, 54º 10' 44'' W). Cultivated *P. latifolia* was obtained from the botanical garden of the University of Santa Maria, RS, Brazil (29° 42' 39'' S, 53° 41' 32'' W). Leaves and flowers of native and cultivated *P. latifolia* were collected in the flowering stage (November-December 2005) from the same population, respectively, and identified by a single author (T. C. D.). Voucher specimens (SMDB 952-954) have been deposited at the Herbarium of the Federal University of Santa Maria.

Chemical analysis

Fresh native (sample A, 100 g) and cultivated (sample B, 100 g) leaves from nine and seven individuals, respectively, and fresh native flowers from four individuals (sample C, 10 g) from *P. latifolia* were subjected to hydrodistillation for 4 h using a modified Clevenger-type apparatus, and followed by extraction with diethyl ether. After solvent removal, crude oil yields were 0.60%, 0.55% and 0.10% (m/m) for samples A {d^{20}: 0.89 g mL^{-1}; η^{20} = 1.4701; $[\alpha]_D^{25}$ = −32.4 (c 0.08, $CHCl_3$)}, B {d^{20}: 0.91 g mL^{-1}; η^{20} = 1.5502; $[\alpha]_D^{25}$ = −30.2 (c 0.10, $CHCl_3$)} and C {d^{20}: 0.85g. mL^{-1}; η^{20} = 1.4821), respectively. Part of the resulting oil (Sample A, 100 mg) was further subjected to column chromatography on silica gel (10 g, 230-400 mesh), eluting with hexane and increasing concentrations of diethyl ether (100%, 98:2, 95:5, 90:10 and 80:20). Ten fractions of about 50 mL each were obtained. Fractions 2 and 3 (100% n-hexane) afforded limonene (15 mg). Fraction 5 (98:2) afforded dihydrocarvone (12 mg), and fractions 6 and 7 (95:5) afforded carvone (35 mg). The identity of the isolated was established by co-injection (GC) with standards available in our laboratories.

The oils were analyzed by GC and GC-MS. GC analyses were performed using a Varian CP-3800 gas chromatograph with a data handling system, FID detector and SE-54 fused-silica column (25 m x 0.25 mm i.d., film thickness 0.25 μm). Operation conditions were as follow: injector and detector temperatures, 220 and 280 °C, respectively; carrier gas, H_2; oven temperature program from 50 °C to 250 °C at 4 °C min^{-1}. GC-MS analyses were performed using a VARIAN model 3800 Saturn system operating in the EI mode at 70 eV equipped with CP-SIL cross-linked capillary columns (25 m x 0.25 mm i.d., film thickness 0.25 μm). The identity of the oil components was established from their GC retention times and comparison of their MS spectra with those reported in the literature,[3] and by computer matching with the Wiley 5 mass spectra library, and as well as by co-injection with standards available in our laboratories whenever possible.

Chiral monoterpene constituents (α-pinene, limonene, *trans*-dyhidrocarvone and carvone) of *P. latifolia* oils were identified by peak enrichment by enantioselective capillary GC with two fused capillary columns, 25 m × 0.25 μm, coated with the new phase heptakis (3-*O*-pentafluoropropionyl-2,6-di-*O*-pentyl)-β-cyclodextrin[17] and octakis(3-*O*-butiryl-2,6-di-*O*-pentyl)-γ-CD (Lipodex- E),[18] each diluted with polysiloxane OV-1701. Varian CP-3800 gas chromatograph was used for the analyses; all runs were performed with the temperature program 35 °C for 15 min, and from 35 °C to 180 °C at 3 °C min^{-1}.

Dihydrocarvones

Dihydrocarvones were prepared from (*R*)-(−)-carvone and (*S*)-(+)-carvone as described previously,[19-20] as a 1:4.5 mixture (65-80 %) of C-1 epimers (*cis*-1,4 and *trans*-1,4, respectively).

Antimicrobial bioassay

The MICs of samples A and B and limonene, carvone, and *trans*-dihydrocarvone, were determined on 96-well culture plates by a micro dilution method using a microorganism suspension at a density of 10^5 CFU mL^{-1} with Casein Soy Broth incubated for 24 h at 37 °C for bacteria, and Sabouraud Broth incubated for 72 h at 25 °C for yeasts. The cultures that did not present growth were used to inoculate plates of

solid medium (Muller Hinton Agar and Sabouraud Agar) in order to determine the minimal lethal concentration (MLC). A collection of eleven microorganisms were used, including three Gram-positive bacteria: *Staphylococcus aureus* (ATCC 6538p), *Staphylococcus epidermidis* (ATCC 12228), *Bacillus subtillis* (ATCC 6633); four Gram-negative bacteria: *Klebsiella pneumoniae* (ATCC 10031), *Escherichia coli* (ATCC 25792), *Pseudomonas aeruginosa* (ATCC 27853) and *Salmonella setubal* (ATCC 19796), and four yeasts: *Saccharomyces cerevisiae* (ATCC 2601), *Candida albicans* (ATCC 10231), *Candida dubliniensis* (Isolated clinical SM-26) and *Cryptococcus neoformans* (ATCC 28952). Standard strains of microorganisms were obtained from American Type Culture Collection (ATCC), and standard antibiotics, chloramphenicol and nystatin, were used in order to control the sensitivity of the microbial test.[21] Proper blanks were assayed simultaneously and samples were tested in triplicate. Technical data have been described previously.[22-24]

Results and Discussion

As shown in Table 1, the qualitative and quantitative composition of samples A, B and C, displayed significant differences. More than 20 components were detected in the essential oils, making up 99.25, 99.26, and 99.23% of the total oil of samples A, B and C, respectively. Monoterpenes (*ca.* 99%), mainly limonene, carvone, and *trans*-dihydrocarvone, were predominant in the essential oils of all the leaves and flowers studied. In leaves of cultivated *P. latifolia* (sample B), *trans*-dihydrocarvone was found in lower abundance (0.66%), while in flowers of native *P. latifolia* (sample C), *trans*-dihydrocarvone was the main component (77.80%) and there was a lower abundance of carvone (4.50%). These monoterpenes are very important to the flavor and fragrance industry. Because the biological activity, smell and organoleptic properties of these compounds are determined by their stereochemistry,[25] in this study the absolute configuration of α-pinene, limonene and carvone was determined by enantioselective capillary gas chromatography using heptakis (3-*O*-pentafluoropropionyl-2,6-di-*O*-pentyl)-β-cyclodextrin[17] as the chiral stationary phase (Figure S1). The absolute configuration of dihydrocarvone was determined by enantioselective chemical transformation of carvone to dihydrocarvone. For this purpose, (*S*)-(+) and (*R*)-(−)-carvones were submitted to reduction with Zn in methanol-water[19,20] to afford a mixture of diastereoisomers of *cis*- and *trans*-dihydrocarvones in a 1:4.5 ratio, respectively (Figure 1), by GC experiment. The four stereoisomers of dihydrocarvone were used as CPGC standards. By comparison of the chromatograms of the standards with the chromatograms of the oils and by co-injection, it was possible to assign unambiguously the absolute configuration of dihydrocarvone as (1*R*, 4*R*)-*trans*. To conduct this study, octakis(3-O-butiryl-2,6-di-O-pentyl)-γ-CD (Lipodex- E)[18] was used as the chiral stationary phase. (Figure S2). All monoterpenes analyzed were present in the oils as only one isomer (ee > 99%). Thus, the absolute configuration of the monoterpenes was determined as (*S*)-(−)-α-pinene, (*S*)-(−)-limonene, (*R*)-(−)-carvone, and (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone.

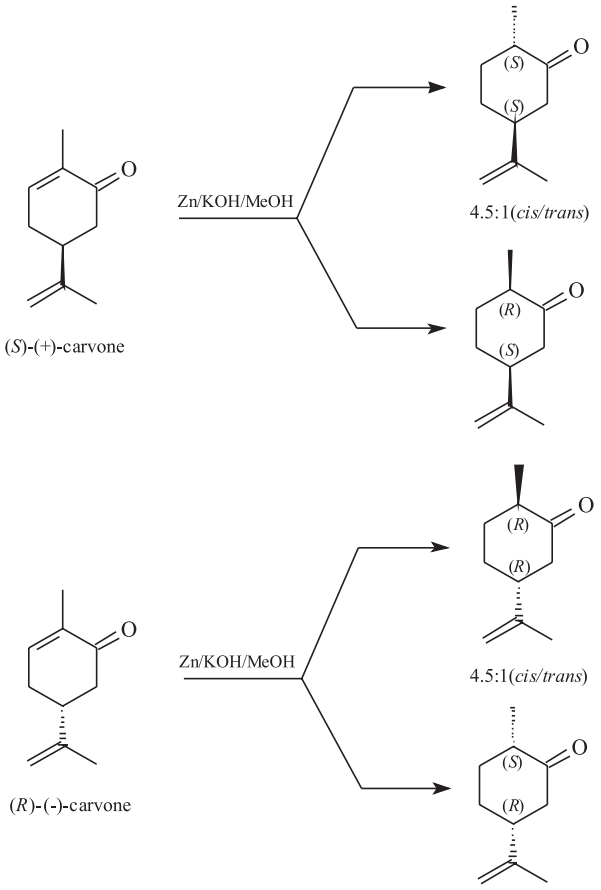

Figure 1. Preparation of dihydrocarvones from (*R*)-(−)- and (*S*)-(+)-carvones.

The antimicrobial activity of the oils and of the isolated (*R*)-(−)-carvone and (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone, was evaluated by determining the minimal inhibitory concentration (MIC). The results, between 1.25-10.0 mg mL^{-1}), showed that the oils of samples A and B, (*R*)-(−)-carvone and (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone have only a modest antimicrobial activity against the tested microorganisms compared to chloramphenicol for bacteria and nystatin for yeasts (Table 2). Because of the small amounts of sample C available, we were unable to obtain information about their antimicrobial activity.

Table 1. Percentage composition of the essential oils of *Poiretia latifolia* Vogel

No.	Component[a]	KI[b]	KI[c]	A	B	C	Identification
	Monoterpene Hydrocarbons			17.35	32.07	16.33	
1	α-Thujene	946	1030	-	0.05	-	-
2	(−)−α-Pinene	940	1020	0.23	0.84		GC-MS, Co
3	Thuja-2,4(10)-diene	959	nd		-	0.02	-
4	Sabinene	970	1042	0.41	0.40	0.63	GC-MS
5	β-Pinene	982	1122	0.56	2.53	-	GC-MS, Co
6	β-Myrcene	985	1160	0.10	0.65	-	GC-MS, Co
7	α-Terpinene	1015	1187	-	-	0.08	GC-MS, Co
8	(−)-Limonene	1018	1206	16.05	27.6	15.60	GC-MS, Co
	Oxygenated Monoterpenes			81.54	67.04	82.30	
9	1-Octen-3-ol	973	1113	0.39	-	-	GC-MS, Co
10	*cis*-Sabinene-hydrate	1068	1199	0.06	0.03	-	GC-MS
11	Linalool	1090	1252	0.09	-		GC-MS, Co
12	α-Thujone	1100	1407	-	0.25	-	GC-MS, Co
13	β-Thujone	1113	1425	-	0.30	-	GC-MS, Co
14	*cis*-Limonene oxide	1123	1430	0.27	-	-	GC-MS
15	Terpinen-4-ol	1179	1460	-	0.02		GC-MS, Co
16	α-Terpineol	1190	1492	-	0.23	-	GC-MS, Co
17	(+)-*trans*-Dihydrocarvone	1193	1595	18.05	0.66	77.80	GC-MS, Co
18	*trans*-Carveol	1207	1604	1.29	1.35	-	GC-MS
19	*cis*-Carveol	1229	1679	0.34	-	-	GC-MS
20	(−)-Carvone	1247	1713	61.05	64.20	4.50	GC-MS, Co
	Sesquiterpene Hydrocarbons			0.28	0.15	0.60	
21	β-Caryophyllene	1420	1888	0.18	0.10	0.60	GC-MS
22	Germacrene D	1482	nd		-	-	GC-MS, Co
23	Bicyclogermacrene	1496	1718	0.10	0.05	-	GC-MS
	Oxygenated Sesquiterpenes			0.08			
24	Caryophyllene oxide	1580	1954	0.08	-	-	GC-MS, Co
TOTAL				99.25	99.26	99.23	

[a]Compounds listed in order of elution from SE-54 column. [b]Kovats Indices determined on an apolar SE-54. [c]Kovats Indices determined on a polar PEG-20M column. nd: not identified. Co: peak identifications are based on standard comparison with relative retention time. A: leaves from native *P. latifolia.* B: leaves from cultivated *P. latifolia*. C: flowers from native *P. latifolia*.

Table 2. Antimicrobial activity (MIC and MLC, in mg mL^{-1}) of the oils of *Poiretia latifolia* and of carvone and dihydrocarvone

Microorganism	Sample A		Sample B		(*R*)-Carvone		Dihydrocarvone		control[a]
Bacteria	MIC	MLC	MIC	MLC	MIC	MLC	MIC	MLC	MIC
S. aureus	1.3	10.0	2.5	10.0	2.5	10.0	5.0	20.0	6.3×10^{-3}
S. epidermidis	5.0	5.0	5.0	5.0	5.0	5.0	10.0	> 20.0	6.3×10^{-3}
B. subtilis	5.0	5.0	5.0	5.0	5.0	5.0	10.0	> 20.0	3.1×10^{-3}
E. coli	5.0	> 20.0	5.0	> 20.0	5.0	> 20.0	10.0	> 20.0	3.1×10^{-3}
S. setubal	1.3	2.5	1.3	2.5	1.3	2.5	5.0	> 20.0	3.1×10^{-3}
K. pneumoniae	5.0	5.0	2.5	2.5	2.5	2.5	10.0	> 20.0	3.1×10^{-3}
P. aeruginosa	5.0	5.0	5.0	5.0	5.0	5.0	20.0	20.0	3.1×10^{-3}
Yeasts	MIC	MLC	MIC	MLC	MIC	MLC	MIC	MLC	MIC
C. albicans	2.5	10.0	2.5	10.0	2.5	10.0	2.5	10.0	10.3×10^{-3}
S. cerevisiae	2.5	2.5	2.5	5.0	2.5	5.0	10.0	20.0	10.3×10^{-3}
C. dubliniensis	2.5	5.0	2.5	5.0	2.5	10.0	10.0	10.0	10.3×10^{-3}
C. neoformans	2.5	5.0	2.5	5.0	5.0	20.0	10.0	10.0	5.2×10^{-3}

[a]Standard antibiotic chloramphenicol for bacteria and nystatin for yeasts.

Conclusions

In conclusion, this study present *P. latifolia* as a new source of (*R*)-(−)-carvone, and of (1*R*, 4*R*)-*trans*-(+)-dihydrocarvone, which were present at levels more than 60% in leaves and flowers of *P. latifolia*, respectively. It was observed that resolution of limonene, carvone and dihydrocarvone could successfully be achieved using the stationary phases described here.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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References

1. Müller, C.; *MSc Thesis*, Universidade Estadual de Campinas, Campinas-Brazil, 1984.
2. Janke, H.; Oliveira M. L. A. A.; Siqueira, N. C. S.; *O Gênero Poiretia VENT. no Rio Grande do Sul – Taxonomia e Aspectos Farmacognósticos,* Iheringia, Série Botânica: Porto Alegre, Brasil, vol. 38, p. 43, 1988.
3. Adams, R. P.; *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*, Allured Publishing Corporation: Illinois, USA, 1995.
4. Helader, L. M.; Alakomi, H.-L, Latva-Kala, K.; Mattila-Sandholm, T.; Pol, I.; Smid, E. J.; Gorris, L. G.; von Wright, A.; *J. Agric. Food Chem.* **1998**, *46*, 3590.
5. Oosterhaven, K.; Poolman, B.; Smid, E. J.; *Ind. Crops Prod.* **1995**, *4*, 23.
6. Naigre, R.; Kalck, P.; Roque, C.; Roux, I.; Michel, G.; *Planta Med.* **1996**, *62*, 275.
7. Smid, E. J.; De Witte, Y.; Gorris, L. G. M.; *Postharvest Biol. Technol.* **1995**, *6*, 303.
8. Salom, S. M.; Gray, J. A.; Alford, A. R.; Mulesky, M.; Fettig, C. J.; Woods, S. A.; *J. Entomol. Sci.* **1996**, *31*, 453.
9. Tripathi, A. K.; Prajapati, V.; Kumar, S.; *J. Econ. Entomol.* **2003**, *96*, 1594.
10. Bouwmeester, H. J., Davies, J. A. R., Toxopeus, H.; *J. Agric. Food Chem.* **1995**, *43*, 3057.
11. Bailer, J.; Aichinger, T.; Hackl, G.; Hueber, K.; Dachler, M.; *Ind. Crops Prod.* **2001**, *14*, 229.
12. Faber, B.; Bangert, K.; Mosamdl, A.; *Flavour Fragr. J.* **1997**, *12*, 305.
13. Rani, K.; Akhila, A.; *Fitoterapia* **1998**, *69*, 337.
14. Ringer, K. L.; Davis, E. M.; Croteau, R.; *Plant Physiol.* **2005**, *137*, 863.
15. Carter, O. A.; Peters, R. J.; Croteau, R.; *Phytochemistry* **2003**, *64*, 425.
16. Shimoda, K.; Hirata, T.; Noma, Y.; *Phytochemistry* **1998**, *49*, 49.
17. Mallmann, A. S.; *PhD Thesis,* Universidade Federal de Santa Maria, Brazil, 2008.
18. König, W. A.; Icheln, D.; Runge, T.; Pforr, I.; Krebs, A.; *HRC- J. High Resolut. Chromatogr.* **1990**, *13*, 702.
19. Fairlie, J. C.; Hodgson, G. L.; Money, T.; *J. Chem. Soc. Perkin Trans. 1* **1973**, 2109.
20. Faria, M. L.; Magalhães, R. A.; Silva, F. C.; Matias, L. G. O.; Ceschi, M. A.; Brocksom, U.; Brocksom, T. J.; *Tetrahedron: Asymmetry* **2000**, *11*, 4093.
21. FDA: *Code of Federal Regulations* **1991**, *21*, 300.
22. Hammer, K. A.; Carson, C. F.; Riley, T. V.; *J. Appl. Microbiol.* **1999**, *86*, 985.
23. National Committee for Clinical Laboratory Standards: *Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria that Grow Aerobically,* 5 ed.; Approved Standard NCCLS Document M7-A2: Wayne, PA, 2002.
24. National Committee for Clinical Laboratory Standards: *Reference Method for Broth Dilution Antifungal Susceptibility Testing of Yeasts,* 2th ed, Approved Standard NCCLS document M27-A2: Wayne, PA, 2002.
25. Sousa, D. P.; Nóbrega, F. F. F.; Almeida, R. N.; *Chirality* **2007**, *19*, 264.

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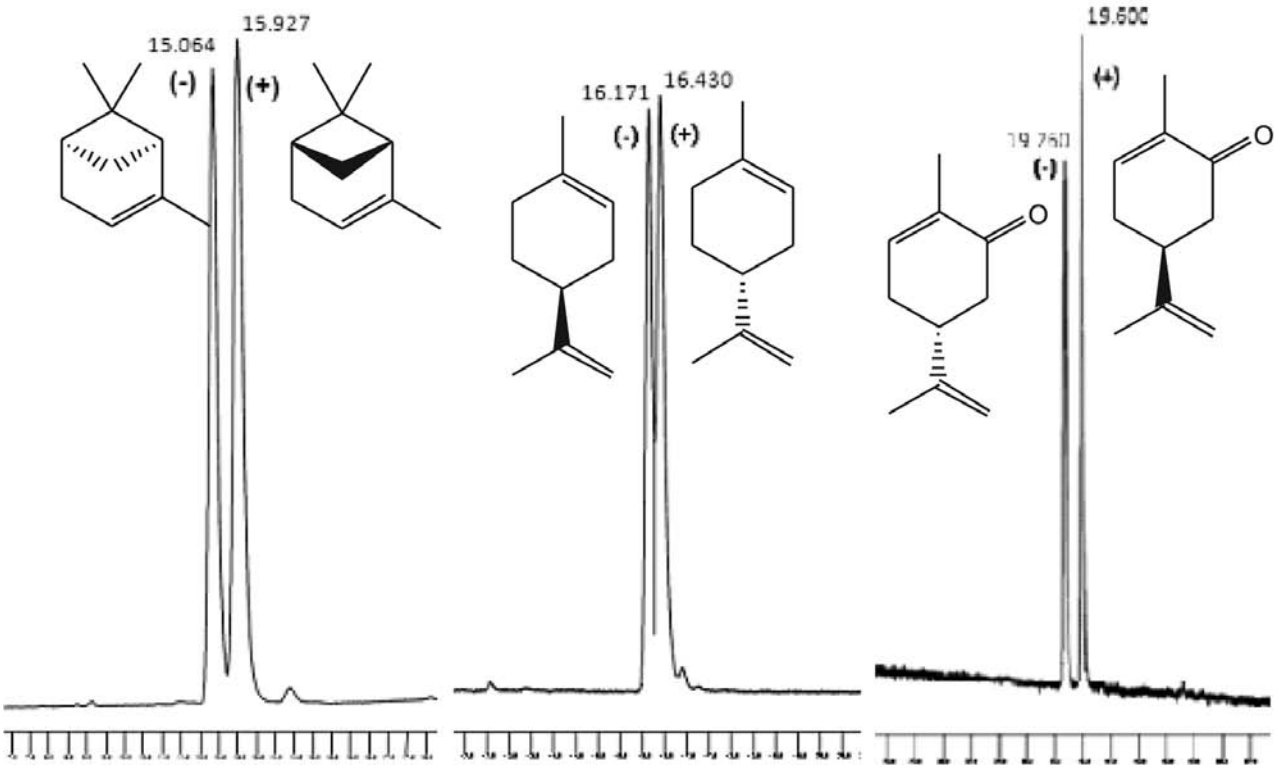

Figure S1. Enantiomer separation of (+/−)-α-pinene, (+/−)-limonene and of (+/−)-carvone on a 25 m x 0.25 mm CCSF coated with Heptakis(2,6-di-*O*-pentyl- 3-*O*-pentafluoropropionyl-)-β-cyclodextrin in OV1701; carrier gas, hydrogen 7 psi.

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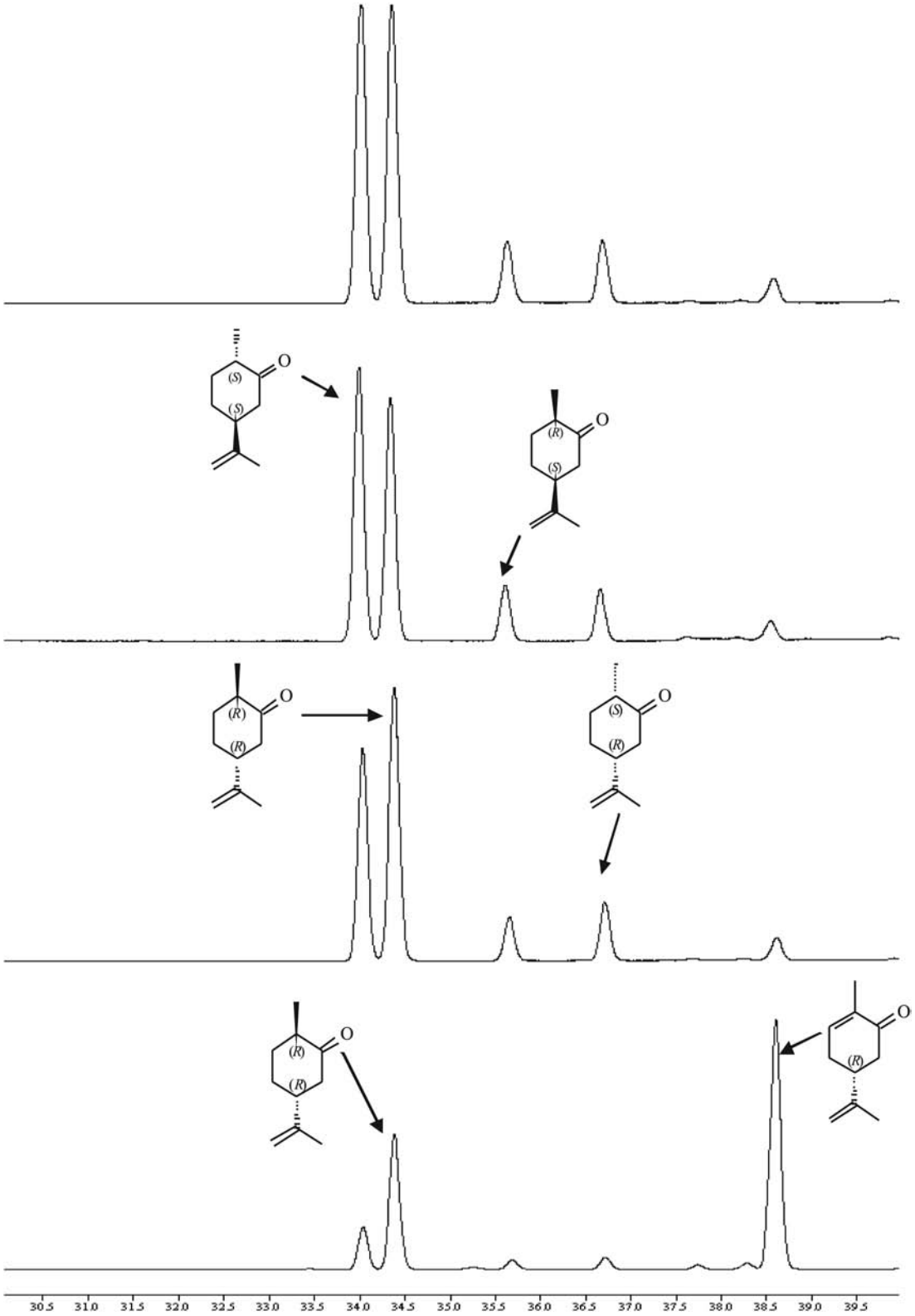

Figure S2. Enantiomer separation of: a) dihydrocarvones from reduction of (*R*)-(−)-and (*S*)-(+)-carvones, b) dihydrocarvones from reduction of (*R*)-(−)-and (*S*)-(+)-carvones + reduction of (*S*)-(+)-carvone, c) dihydrocarvones from reduction of (*R*)-(−)-and (*S*)-(+)-carvones + (*R*)-(−)-carvone , and d) dihydrocarvones from reduction of (*R*)-(−)-and (*S*)-(+)-carvones + essential oil of *P. latifolia* on a 25 m x 0.25 mm CCSF coated with octakis(3-O-butiryl-2,6-di-O-pentyl)-γ-CD (Lipodex- E) in OV1701; carrier gas, hydrogen 7 psi.